SYNOPSIS

'Synthesis and Charge Transport Study of Poly (o-methyl aniline) and Poly (o-ethylaniline)'

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Introduction

Traditionally polymers which are commonly known as plastics are composed of simple repeating molecular units called monomers. The name "Polymer" is derived from the Greek words 'poly' and 'mer' which means many and part respectively [1]. They have been seen as good electrical insulators and most of their applications had relied on their insulating properties [2]. However, until three decades ago researchers showed that certain class of polymers exhibits semiconducting properties [3]. In 1958, Polyacetylene was first synthesized by Natta et al., as a black powder and found to be a semiconductor with conductivity in the range of 10^{-11} to 10^{-3} S/cm [4]. This discovery was followed by the work of Shirakawa and his co-workers in 1977 who reported the synthesis of doped polyacetylene which was formed accidently [5]. This incidence took place when one of the co-workers mistakenly added excessive amount of catalyst in the reaction vessel for the polymerization of acetylene. This resulted in the formation of a silver film instead of the expected black powder. The new product when examined showed extremely different optical properties compared to the normal black powder [5]. The discovery propelled the thrust of researchers in this area which resulted in extensive performance in the field of conducting polymers, MacDiarmid, Heeger and Shirakawa were awarded the Nobel Prize in chemistry in the year 2000 for the discovery of conductivity in polymers [6]. Since this discovery reported by Shirakawa and co-workers, Conducting polymers (CPs) have received much attention in the field of science due to their various physical, chemical properties and numerous possible applications [7]. Conducting polymers sometime called smart polymers are different greatly from insulating polymers because these are conducting. These conducting polymers are organic polymers inherently conducting in nature because of the presence of conjugated π–electrons in the system resulting potential applications due to its low energy optical transition, low ionization potential and a high electron affinity [8-10]. The most widely studied CPs are poly (p-phenylene), poly phenylene vinylene, poly thiophene, polypyrrole, poly isothia naphthene and polyaniline (PANI). They are conjugated that is, they have π-electron delocalisation along their polymer backbone, hence giving them unique optical and electrical properties. These conducting polymers have commonly been used in scientific and industrial studies and in various applications as rechargeable batteries [11-12], sensors [13-17], diodes, in transistors and micro-electronic devices etc. [18].

Literature Review

Among the conducting polymers, polyaniline are considered to be one of the most promising class of organic conducting polymers due to their easy doping/dedoping, good environmental stability, thermal stability, novel properties and potential applications [19-21]. The process of optimizing synthesis parameters, dopability of conjugated polymers and their chemical modification made conducting polymers more applicable and versatile unlike inorganic metals and semiconductors. A numbers of papers are available reporting the synthesis of polyaniline using different dopants and its characterization with numerous applications [22-26]. However, a major problem lies in its poor mechanical properties and processibility. Thus, to use PANI frequently is due to its poor insoluble nature in common organic solvents [27]. This problem has been rendered by using substituted derivatives of anilines simply by incorporating polar functional groups on the polymer backbone such as poly o-toluidine, polyanisdines, poly (N-methyl anilines), poly (ortho-ethyl aniline) etc. The substituted polymers exhibit greater solubility but reporting low conductivity. Different functionalized protonic acids have been introduced, which upon doping makes them conducting and more soluble in common organic solvents [28-29].

Polyaniline has a complex molecular structure existing in three well defined oxidation states namely: leucoemeraldine, emeraldine and pernigraniline [30]. The aniline polymers have the general formula shown in Figure 1 consisting of benzenoid and quinoid units [31-33]. Thus, aniline polymers are basically poly (p-phenyleneimineamine)s, having a chemically flexible -NH group in the polymer chain flanked by phenyl rings on either sides [31-33]. PANI's properties are determined by the regular structure of polymer chains. The existence of each of the three distinct PANI oxidation states based on the value of y [34-35] is shown in Figure 1. The pale yellow colour leucoemeraldine (LE), the completely reduced form of PANI, exhibits when the oxidation state corresponds to y=1. Second is the 50% oxidized or reduced form of PANI polymer with blue colour called as "emeraldine base" (EB) where y=0.5.The completely oxidized formof PANI with blue/violet colour called as "pernigraniline" (PE) can be obtained by putting y=0 in the general formula [34].

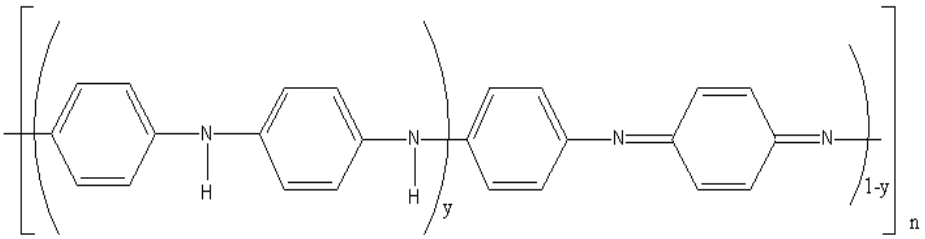

Figure1: Polyaniline general formula consisting different oxidation states: (y =1: leucoemeraldine, y = 0.5: emeraldine, y=0: pernigraniline).

Among various possible oxidation states of PANI "emeraldine base" (EB) is regarded as the most useful form as it can be converted to a green coloured emeraldine salt (ES) of polyaniline by protonation/doping process which is stable at room temperature and shows a considerable conductivity [36-37]. As reported in research papers by different author's properties of polyaniline are summarized as below:

i. Ease of synthesis
ii. It is the only conducting polymer whose electronic structure and electrical properties can reversibly be controlled by both oxidation and protonation
iii. Ease of non-redox doping by protonic acids
iv. It has interesting electrochemical behaviour
v. It shows good environment stability etc.

Research Gap Identification

The exciting and emerging field of organic semiconductors with an emphasis on conductivity in these materials rekindle our interest to explore conducting polymers. Among the CPs family, we have focussed to work on polyaniline polymer and its substituted derivatives, after gaining knowledge from the vast literature survey on them. Different research papers have reported PANI's with different oxidant to monomer ratios and using different dopant conditions for oxidative polymerization of PANI. However, conducting polymers are usually insoluble and infusible because of their rigid conjugated main chain, which limits their application**.** There are several strategies to solve the problems such as attaching appropriate flexible side chains (substituent's) can make the conjugated polymers soluble in organic solvents and thus improving the process ability of conducting polymers has paved the way for large-scale applications of conducting polymers [38-39].

Objectives

We have selected two substituted polyanilines for our study, as study revealed that there is less work reported on these conducting polymers. So the following are the objectives:

i. Synthesis, optimization and Characterization of the polymeric samples.
ii. Electrical conductivity measurements to explain the charge transport behaviour in polymers
iii. To study the effect of dopants on the charge transport behaviour in polyaniline family.
iv. To study the effect of substituent's groups on the charge transport behaviour.
v. The study of its sensing properties for application as humidity sensor.

Polyaniline is promising and exclusive member of the conducting polymer family. PANI referred to as aniline black was initially discovered in 1834 by Runge [40] and investigated in detail by Fritzsche [41] and further, this material was analyzed by Letheby as the non-conducting, highly-coloured polymer known today as semiconducting emeraldine base. It was identified in the past as “indigo” and used as dye for clothes in 1862 [42]. MacDiarmid and Chiang discovered that emeraldine base salt can become conducting after a protonic acid doping [43]. Furthermore, MacDiarmid and co-workers developed in late 1980s the chemical oxidative polymerization method which involves the use of a strong oxidating agent used as catalyst for reaction along a suitable protonic acid, acting as dopant. Employing this method, it is possible to obtain doped PANI as protonated emeraldine salt, which exhibits conductivity as high as 100 S/cm [44]. A. J. Epstein et al., in 1987 showed the emeraldine base form of polyaniline can be varied from insulating (10^{-10} S/cm) to conducting ($\sim 10^{+1}$ S/cm) through protonation [2]. Surville et al., in 1968 reported proton exchange and redox properties of PANI [45]. PANI consists of complex molecular structure composed of reduced benzenoid units and oxidized quinoid units showing a mixed oxidation state polymer [46]. In 1992, Y. Cao et al., reported PANI doped with camphor sulfonic acid (CSA) with electrical conductivity much higher than that of PANI doped with inorganicacids [29]. J. Laska et al., in 1995, demonstrated that the protonation of polyemeraldine base with aryl phosphoric acid

diesters constitutes an excellent group of polyanilines dopants which not only made this polymer conductive but a polymer with good thermal properties [47].

During the last two decades, much research has been devoted to quasi-one-dimensional polymers having an extended π-electron system. The investigation of these semiconductor polymers has become increasingly important because of their unusual combination of electronic properties [48-49]. M.E. Vaschetto et al., in 1999 studied the electronic properties of conducting polymers containing phenylene rings. It was found that by replacing a carbon atom by a nitrogen atom in the phenylene ring, an occupied π -band appears. Simultaneously, the first ionization potential increased which can be related to the electronegativity of nitrogen compared to that of carbon. This caused to increases the π-electron delocalization and produced a stabilization of the system [50]. Shoji et al., in 1998 studied the effect of sulfonic group on conducting polyaniline prepared by synthetic method. The emeraldine salt was sulfonated by chlorosulfonic acid in dichloroethane at 80°C and subsequently hydrated in water at 100°C. It showed that conductivity value for pellet decreased from 0.023 to 1.7×10^{-5} S/cm,due to the reduced π- conjugate ion by sulfonation as its electron withdrawing group, steric repulsion among them and cation radicals created by doping turn out to unstable [51]. Otakar et al., in 1998 reported that PANI powder particle organize themselves in to chain under the effect of weak electrical field strength on powder conductive polyaniline when dispersed with in a non-conducting liquid,1,2,4-trichlorobenzene(TCB) due to the interaction of induced dipole. It was also found that when voltage or the concentration of suspension particles was increased, the current grew more quickly in the beginning and its steady value was considerably higher [52]. Electrical conductivity of PANI was found to be 10^{-3} to10^{-2} S/cm when protonic acid employed as counter-anion has shown excellent electrochemical redox reversibility in non-aqueous system. The reason was due to ethylene oxide oligomers contained in doped PANI showed excellent ion transfer media [53].

J. Prokes et al., in 2004 studied the effect of organic and inorganic acids on the polyaniline preparedby the oxidative polymerisation with ammonium peroxydisulfate. Results showed an amorphous and semi-crystalline nature of polyaniline at temperature 20°C and 50°C respectively, while conductivity of the PANI pellets showed best results with methane sulfonic and hydrofluoric acid samples [54]. H. Qiu

et al., in 2005 studied HCl doped polyaniline prepared by using a solution polymerization process, in pellet form. The samples showed that conductivity decreased sharply when the annealing time reached 30 min and then decreased gradually with further increase in annealing time. The degradation of the conductivity is mainly attributed to the loss of chlorine as the effective dedoping occurred due to the chlorination of the rings in the polyaniline pellets [55]. D.W. Gu et al., in 2005 were emphasized the importance of PANI film, as the electronic applications of the material, as well as experimental study, usually need a suitable means, by which the material may be easily formed in thin film by spin-casting method. The conducting PANI films were synthesized on glass substrate by in situ polymerization under very high pressure. It was observed that when very high pressure is used in polymerization, the value of conductivity increases. Because protonic acid doping of emeraldine base units with 1M aqueous HCl resulted in complete protonation of the imine nitrogen atoms to give the fully protonated PANI. There was a correlation between the conjugation and the conductivity of PANI which showed that the decrease of conductivity was associated with the decrease in conjugation length. This meant that each conjugation breaking defect could induce more charge localization and make charge transport more difficult. Thus conjugation length in PANI films was increased and the more charge delocalization was induced, which made the charge transport easier [56].

N. Bicak et al., in 2005, showed that thin polyaniline film prepared using new ionic liquid, 2-hydroxyethyl ammoniumformate (HAF), at lower temperature ~ 0°C results in highly conducting PANI with a conductivity of 37S/cm, when doped with PTSA [57]. R. Madathil in 2005 studied about the conductivities of the polyaniline bulk films consisting nano fibers by using a four-point probe method at ambient temperature. Thin films of polyaniline oligomers showed conductivity of 30 S/cm. It was found that films doped with HCl and HNO_3 exhibited high conductivities. The characteristics of dopant anions such as their electron affinity, size and their orientation with respect to PANI chains can cause variation in conductivities. But HBr,H_2SO_4 and methane sulfonic acid reported low conductivities, the major factor considered to be the bulkiness of these dopant anions [58]. J.S. Li et al., in 2006 studied the formation of PANI films on the quartz substrates under high pressure (>100MPa) which caused the enhancement of conjugation length and the

improvement of electrical contact between the fibrils. It showed that the electrical property of PANI films improved by VHP synthesis [59].

Although PANI can be synthesized easily by chemical oxidation of aniline, PANI is not generally processable due to its less solubility for almost all the solvents which hinders its versatility in application domain [60-61]. Work has been done to improve processability while maintaining the inherent properties of PANI, it was well-known to combine PANI with other processable polymers such as polystyrene, polyvinylchloride (PVC) etc. and to use an anionic surfactant as a dopant such as dodecylbenzenesulfonic acid (DBSA) etc. [60,62]. So that to make technological conducting PANI blends or PANI composites applicablein many fields. J. Laska et al., in 1997 investigated different polyanilineblends. Plasticized protonated polyaniline made by phosphoric acid diesters serve as a conductive additive to common polymer such as poly (vinyl chloride), polystyrene, poly (methyl methacrylate) and cellulose derivatives. Found that the conductivity of the blends ranges between $10^{-2}$and 10 S/cm. However conductivity of the blends depends on several factors such as processing, temperature, content of the doping agent, content of the conducting phase in the non conducting matrix and quantities of the PVC plasticizers. The conductivity value of the cellulose blends containing 5% of polyaniline was found to be 10^{-3} S/cm [62]. J. Stejskal et al., in 2003 reported the chemical oxidative polymerization of polyaniline in an aqueous medium containing an anionic surfactant-sodium is (2-ethylhexyl) sulfosuccinate,dodecylbenzenesulfonic acid and its sodium salt, and sodiumdodecylsulphate. Showed better electrical stability of polyaniline [63]. Polyaniline salts were studied as polyaniline-dodecylhydrogensulfate-sulfuric acid (PANI-DHS-H_2SO_4),polyaniline-dodecylhydrogensulfatenitric acid(PANI-DHS-NO_3) and polyaniline-dodecylhydrogensulphate hydrochloric acid salt (PANI-DHS-HCl) in chloroform synthesized by chemical oxidative polymerization of aniline using pyridinium chloro chromate (PCC) as an oxidizing agent in aqueous organic medium in the presence of mineral acid and sodiumdodecylsulfate (SDS) surfactant Polymerization caused incorporation of both acid and surfactant groups into the polyaniline chain as dopants, showed excellent yield (1.25g) and conductivity (0.1S/cm) for PANI-DHS-HCl [64]. L.F. Malmonge et al., in 2006 reported about electrically conductive poly (vinylidenefluoride) (PVDF)–polyaniline blends of different composition synthesized by chemical polymerization of aniline in a mixture

of PVDF and dimethylformamide (DMF). The electrical conductivity showed a great dependence on the syntheses parameters because only few oxidant/aniline molar ratio equal to ~1 and p-toluenesulfonic acid–TSA/aniline ratio between 3 and 6 showed higher value of the electrical conductivity. Also characterization techniques strengthen the fact that the PANI is responsible for the high electrical conductivity of the blend [65]. J.C. Xu et al., in 2005 studied PANI/TiO_2 composites prepared by in situ polymerization.TiO_2 nanoparticles with an average diameter about 20 nm were used as a dopant of polyaniline. It was found that the conductivity of composites at low TiO_2 content showed much higher value than that of neat PANI, but reverse result obtained with the increasing contents of TiO_2. This attributed to the doping effect associated with TiO_2 nanoparticles caused to made a more efficient network for the charge transport, thus enhancing the conductivity of the composites [66].

N. Ballav et al., in 2006 studied composites of polyaniline with MoO_3 prepared via polymerization of the respective monomer by ammonium vanadate (AV)/H_2SO_4 oxidant system in presence of an aqueous suspension of MoO_3. Dc conductivity values of PANI–MoO_3 composites were found to be in the order of 10^{-2} S/cm [67]. S. De et al., in 2007 studied the nano composites of conducting polyaniline and layered vanadyl phosphate, $VOPO_4.2H_2O$ synthesized by redox intercalation method. Intercalation and polymerization of aniline occurred through redox reaction. These polyaniline molecules are ordered and are electronically conducting, which caused to improve the conductivity [68]. A.P. Sobha et al., in 2014 studied nanocomposites consisting of functionalized multi-walled carbon nanotubes and polyaniline prepared by traditional in-situ polymerization and dynamic interfacial polymerization methods. The highly extended and well-aligned PANI chain structure increased the effective degree of electron delocalization between $\pi-$ bonds in aromatic rings of PANI and graphitic structure of nanotubes and, therefore, enhanced the carrier mobility in PANI, which caused to enhance their electrical conductivity [69]. Machappa et al., in 2015 studied about the conductivity behaviour of PANI/$MgCrO_4$ composites synthesized by using in situ polymerization of polyaniline in presence of magnesium chromate. The composites were synthesized with various compositions of $MgCrO_4$ in PANI. It was found that the rapid increase in ac conductivity for certain value due to the extended chain length of polyaniline which facilitates the hopping of charge carriers when the content of $MgCrO_4$ is up to 30 %

[70]. Q.Yan et al., in 2016 studied eco friendly and highly efficient dopant tea polyphenol (TP) with PANI. Result showed that solubility of PANI doped with TP increased because chains enhanced the π–π* interaction and facilitated the electron delocalization [71]. A considerable amount of interest generated in studying π-conjugated polyaniline, unique member of the polymer family, becoming indispensible for this century. But it shows poor processibility due to its insolubility in common organic solvents, due to the stiffness of its backbone [72]. This disadvantage restricted its use in industrial/commercial applications. This problem has been overcome, as researcher took some unique path by using substituted derivatives of anilines such as toluidine, N-ethyl anilines,ortho-ethyl aniline etc .[73-76]. In order to obtain additional insight into polyaniline, methyl substituent has been used to block the ortho position of aromatic ring of aniline. It may be remarked that methyl-substituted aniline called o-toluidine has been found to have additional advantage over polyaniline due to its fast switching time between the oxidized and reduced states. POT was chosen as the conducting polymer owing to its higher processibility as well as solubility as compared with PANI [77]. MacDiarmid et al., investigated Poly (o-toluidine) as an electrically conducting polymer, which is emerging as a promising synthetic metal.

The possibility of synthesizing and doping of Poly (o-toluidine) with protonic acid dopants containing different types of counter ions is one of the key factors responsible for the versatility of this class of polymers [78]. M. Wan et al., in 1995 showed that the conductivity of poly (o-methyl aniline) or poly (ortho-toluidine), in which $–CH_3$ group is introduced to the benzene rings on the emeraldine chain of polyaniline, at room temperature is one or two orders of magnitude lower than that of PANI. Reduced conductivity is due to decrease in conjugation extent, hence electron delocalization resulting decrease in transport speed of charge carriers along and across the polymer chain. Result was also strengthened by UV-Vis absorption spectra, X-ray photoelectron spectroscopy, cyclic voltammograms and decomposition of the ESR signal, X-ray diffraction and temperature dependence of conductivity [79]. Most of the interesting chemistry and physics of conducting polymers are associated with the electronic structure at the π-levels at the valence and conduction band edges. By doping the conjugated polymer, a charge transfer is introduced through either oxidation or reduction (n or p-type of doping). In the case of PANI, doping is

achieved by protonation of backbone nitrogen sites. Thus the total electron number does not change but vacancies (on two sites) are created [80-81]. M.V. Kulkarni et al., in 2004 studied the synthesized polyaniline and poly (o-toluidine) doped with p-toluene sulphonic acid (PTSA) by in situ chemical polymerization method using ammonium per sulphate as an oxidizing agent. The less conductivity in poly (o-toluidine) is due to the cumulative steric as well as electronic effects of the bulky methyl substituent present on the benzene ring [82]. M. V. Kulkarni et al., in 2005 studied synthesized substituted polyaniline, poly (o-toluidine) by oxidative chemical polymerization method, but used different dopants namely: acetic, formic and oxalic acids during the polymerization process. The percentage yield as well as conductivity is found to be higher in formic acid doped polymer than that doped with acetic and oxalic acid. However, increase in conductivity with temperaturewas observed in all the polymers [83]. B. Gercek et al., in 2007 studied four derivatives of PANI namely: poly (o-toluidine), poly (N-methyl aniline) (PNMAn), poly (N-ethyl aniline) (PNEAn), and poly(2-ethyl aniline) (P2EAn). POT was found to have the highest conductivity with a value of 6.87×10^{-7} S/m, and P2EAn has the lowest with 1.01×10^{-7} S/m, among the polyaniline derivatives examined [84].

Synthesis of polyaniline by chemical oxidative polymerization with poly (m-nitroaniline), poly (m-chloroaniline) and poly (o-methyl aniline) was studied. Different properties were measured and compared with PANI to find out the effect of electron donating groups—CH_3 and electron withdrawing groups (—Cl, —NO_2). It was observed that presence of substituents on the benzene ring of aniline reduces the yield and increases the solubility, thermal stability and electrical conductivity depending on the type of substituent's [85]. S.M. Ebrahim et al., in 2010 studied the synthesized POT doped by dodecylbenzene sulfonic acid oxidative polymerization technique. Studies revealed that, highest conductivity of POT-DBSA (1.88×10^{-3} S/cm) was obtained at 1:1 molar ratio of oxidant to o-toludine [86]. H. F. Hussein et al., in 2011 studied synthesis of poly (o-toluidine) doped by p-toluene sulphonic acid by using oxidative chemical polymerization method. It was found that conductivity values of this polymer increased with temperature up to 2.46×10^{-5} S/cm [87]. K. M. Ziadan et al., in 2012 studied substituted poly (o-toluidine) synthesized by chemical polymerization method used ammonium per sulphate as oxidizing agent. Thin films of poly (o-toluidine) have been prepared by spin coating method. The

studies revealed that electrical conductivity increases with temperature from 1.49×10^{-7} S/cm at 293K to 6×10^{-6} S/cm at temperature 383K. This behaviour indicates that the POT polymer behaves as semiconductor material [88]. M. K. Sahoo in 2013 studied about the o-methyl aniline/carboxylic acid-functionalized multiwalled carbon nanotubes (c-MWCNTs) nanocomposites and it was found that the electrical conductivity of the nanocomposites increased due to the interaction between polymer and nanotubes that enhanced electron delocalization [89]. O. Melad et al., in 2014 studied synthesizedpoly (2-methyl aniline-co-aniline) at different molar ratios of the monomers [90]. R.A.Mishra et al., in 1999 studied different properties of poly (2-ethylaniline), a π-electron conjugated conducting polymer prepared under different polymerization conditions in nitrogen atmosphere. It was found that solvents and electrolytes affected the yield as well as electrical conductivity in the range of 10^{-4} to 10^{-7} S/cm due to the variation of the chain length of the polymer. It was observed that dopant oxidation level and method of synthesis causes degradation in the electrical conductivity [76].

Kaufman et al., in 1980 showed a model for charge transportation through polymeric films in the sense that propagation of charge takes place by auto exchange electronic reactions among oxidized and reduced species positioned at neighbouring sites in the film [91]. A. L. Schemid et al., in 2000 used this model to study poly (2-ethyl aniline) when mineral acids are used. The electrochemical response of poly (2-ethylaniline) depends on the charge/size ratio of the counter ion due to both steric and electronic effects. It was found that a large substituent influences the participation of anion in the ionic exchange process due to steric hindrance. The electron-donating effect of the ethyl substituent is completely disregarded in comparison to thesteric effect that produces an increase of the torsion angle between phenyl rings, leading to the polarization of the first oxidation peak of the 2-ethyl polyaniline film [92]. However, in conducting polymers, the polymer backbone is extensively conjugated, which makes charge delocalization possible considerably.Various models have been developed to explain the mechanism of charge transport in conducting polymers. C.O. Yoon et al., in 1996 studied the electrical transport properties of PANI prepared by chemical oxidative polymerization in the presence of phosphoric acid under low temperature and used a variable range hopping (VRH) model, to find the better conductivity value. The freshly prepared emeraldine salt form of the polyaniline

showed relatively high electrical conductivity of ~40S/cm at room temperature. The transport data of phosphoric-acid-doped polyaniline suggested that homogeneity of the material is in such a degree that the charge transport can occur both through hopping between partially disordered states and through diffusion between partially metallic states [93]. J. Huang et al., in 1998 reported the temperature and pressure dependence of conductivity in polyaniline doped with β-naphthalene sulfonic acid (NSA). The temperature dependence of the conductivity for both granular and tubular PANI-NSA can be interpreted within the one dimensional variable range hopping (1D-VRH) model [94]. F. Gmati et al., in 2007 studied PANI, doped with dichloro acetic acid (DCA) and trichloro acetic acids (TCA), respectively at various doping rates. The results of this study indicated better chain ordering and higher conductivity for PANI doped with TCA. The dc conductivity of all samples was suitably fitted to Mott's three dimensional variable-range hopping model. The direct current (dc) and alternating current (ac) electrical conductivities of PANI salts were investigated in the temperature range 100–310 K [95].

Proposed Methodology

There are several reports available in the literature survey of PANI over the decades about the structural and constitutional aspect of aniline polymerization. Synthesis of PANI by chemical oxidation way involves the use of either hydrochloric or sulphuric acid in the presence of ammonium persulfate as the oxidizing agent in the aqueous medium. The principal function of the oxidant is to withdraw a proton from an aniline molecule, without forming a strong co-ordination bond either with the substrate/ intermediate or with the final product. It is reported by different authors that polymerization process depends on the concentration of monomer, oxidant and dopant. This emphasized the importance of optimization condition during polymerization to obtain polymer.

In our study we will use a chemical oxidative polymerization method for polymer synthesis. For this, first of all we will optimize polymer for oxidant to monomer and dopant to monomer ratios. Polymers shall be doped with different dopants like p-toluene sulphonic acid, camphor sulfonic acid, dodecylbenzenesulfonic acid, teapolyphenol and formic acid etc. Linear four probe method will be used to study the d.c. conductivity and its temperature dependence. UV-VIS, FTIR, XRD and SPM techniques will be used to study the polymer during research work.

Research Plan Schedule

Research Activity	Progress in Months											
	3	**6**	**9**	**12**	**15**	**18**	**24**	**30**	**36**	**38**	**42**	**48**
Course work, extensive literature survey or design of work	Jan 2015 to Jan 2016											
Research gap identification and development of methodology			Sep 2015 to March 2016									
Synthesis and optimization parameter					Jan 2016 to Jan 2018							
Characterization and charge transport study						Dec 2016 to Dec 2018						
Conclusion, manuscript preparation for publication and thesis writing								Jan 2018 to March 2019				

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